



A Comprehensive Review on Zinc Sulphide Thin Film by Chemical Bath Deposition Techniques

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Abstract

Nowadays, the synthesis of metal chalcogenides has received very wide attention because of their suitability, simplicity and cost-effectiveness for large scale deposition by the selection of suitable chemical methods. Predominantly, thin films technology has led to large scale deposition techniques, even though, using the variety of substrates such as insulators, semiconductor or metal. It has associated with these methods at a lower temperature for reduces the chances of oxidation and corrosion of the substrate. Recent days, numerous methods available for the deposition of thin films on the substrate. Among these, Chemical Bath Deposition (CBD) seems to be an attractive one. It gives many numbers of advantages over conventional thin film deposition method. Moreover, it does not require high temperature as well as sophisticated and expensive equipments. Most researchers motivated the metal sulphides. They have a wide range of applications like sensors, modulators, dielectric filters, LEDs, efficient phosphors in flat panel display and buffer layers in the solar cells.

In this present paper describes the comprehensive review on the necessary background theory for the thin film depositions. We discussed the CBD method in details to obtain well-adherent and uniform zinc sulphide (ZnS) thin films. Their bath parameter, structural, morphological, optical, electrical properties etc., are also highlighted.

Keywords: Chemical bath deposition; Metal Chalcogenides; Thin films; Zinc Sulphide.

1. INTRODUCTION

Transition metals with group 16 elements, generally known as metal chalcogenide (Palve *et al.* 2019). Metal chalcogenides are wide band-gap semiconducting materials and metal chalcogenides thin films have number of novelty applications in various fields such as superconducting films, anticorrosive films, diamond films, surface modification, hard coatings, photoconductors, Infrared detectors, solar cells, solar selective coatings, optical imaging, magnetic films, optical mass memories, temperature control of satellites, waveguide coatings, sensors, fabrication of large area photodiode arrays catalyst etc. World widely the usage of thin film based solid state electronic devices rapidly increased as well as they developed for integrated chips for a monolithic and hybrid microelectronics Today, numerous techniques available for the growth/deposition of metal sulphides thin films: vacuum evaporation, electro-deposition, electro conversion, dip growth, spray pyrolysis (Hernández-Fenollosa *et al.* 2008), sputtering, successive ionic adsorption and reaction, chemical bath deposition (CBD) method (Roy

et al. 2006), sol-gel method, solution-gas interface technique, thermal oxidation, molecular beam epitaxy etc. Among these method the chemical vapour deposition (Lee *et al.* 2005), spray pyrolysis (Hernández-Fenollosa *et al.* 2008), vacuum evaporation methods require consciousness of high temperature for specific and useful deposition of chalcogenides thin films. On the other hand, few methods involved in chemical solution method need much low temperature for the successful deposition of chalcogenides thin films. Recently, numerous researcher reported that chemical bath deposition played as major role in deposition of thin films (Biswas *et al.* 2005; Roy *et al.* 2006; Prabahar *et al.* 2009a; Prabahar *et al.* 2009b; Kathirvel *et al.* 2011; Srikanth *et al.* 2011; Jeyachitra *et al.* 2014; Gallanti *et al.* 2016). Because they easily attainable temperature, simple and convenient for large scale deposition as well as inexpensive method.

Many researchers established and reported a versatile and environmental friendly solution approach for the fabrication of a variety of metal sulphide thin films because of the easy availability and low cost of the

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starting materials. Metal hydroxides, metal oxides, metal chlorides, metal acetylacetonates and metal acetates used as the starting materials (Tian *et al.* 2014). They dissolved in thioglycolic acid and ethanolamine, forming many types of metal organic precursor solutions.

In the present paper describes a comprehensive review of recently published research articles towards ZnS thin films deposited by the CBD technique. Subsequently, it provides the major properties of ZnS film and gives the benefits of CBD method for ZnS thin film preparation and observed variations in its properties like film growth rate, crystalline nature, surface morphology, and optical spectra.

2. BASIC PROPERTIES OF ZnS

Among all metal chalcogenide, ZnS is an important semiconductor compound of II–VI group with excellent physical properties and direct wide band-gap energy of 3.7 eV at 300 K, has attracted great attention (Salim *et al.* 2012; Palve *et al.* 2019). It has two basic types: cubic phase (sphalerite) and hexagonal phase (wurtzite). ZnS thin film act as a “Buffer” and “window” layer in heterojunction solar cell. It has numerous applications in optoelectronics (Xiong *et al.* 2004; Daniels *et al.* 2006), solar cells, lasers (Biswas *et al.* 2008), ultraviolet light emitting diodes (Luo *et al.* 2008), as a phosphor host (Wang *et al.* 2000), optical sensors (Biswas *et al.* 2005), luminescence (Zhu *et al.* 2003; Goswami *et al.* 2007), because of high refractive index (2.35) it is used in antireflection and coating (Liu *et al.* 2009) etc.

Table 1. Some Important Parameters and Their Effects on Various Properties of ZnS thin films by CBD method (Sinha *et al.* 2018)

S. No.	Name of the Parameter	Properties of ZnS films
1.	Zinc salt and [Zn]/[S] ratio	Crystalline behaviour, morphology, film growth
2.	Complexing agent	Crystalline behaviour, morphology, optical transmittance, thickness and roughness
3.	Stirring speed	Thickness and roughness, film growth rate
4.	pH value	Crystalline behaviour, optical transmittance, band-gap, film growth rate
5.	Deposition temperature	Thickness, optical transmittance, band-gap, pH of solution, morphology
6.	Deposition time	Crystalline behaviour, thickness, band-gap
7.	Humidity	Crystalline behaviour, morphology, optical transmittance
8.	Annealing	Crystalline behaviour, morphology, optical transmittance

Table 2. Properties of ZnS (Navneet *et al.* 2016)

Name of Property	Name of the parameter	Parameter value
Chemical Properties	Chemical formula	ZnS
	Molecular weight	97.46 g/mol
	Group	Zinc-12
		Sulphur-16
	Crystal Structure	Cubic
Electric Properties	Lattice Constant	5.4093 Å
	Dielectric Constant	8.9
	Electronic configuration	Zinc:[Ar] 3d ¹⁰ 4s ²
		Sulphur:[Ne] 3s ² 3p ⁴
	Band Gap	3.54 eV
Thermal Properties	Electron Mobility	180 cm ² /Vs
	Hole Mobility	5 cm ² /Vs
	Heat of Fusion	390 J/g
	Heat of Formation	477 KJ/mol
	Thermal coefficient of Expansion	6.36 µm/m°C
Mechanical Properties	Thermal Conductivity	25.1 W/mK
	Specific heat capacity	0.472 J/g°C
	Density	4.079 g/cm ³
	Boiling Point	1185 °C
	Melting Point	1850 °C
Optical Properties	Flexural Strength	103 MPa
	Modulus of Elasticity	75 GPa
	Poisson's Ratio	0.27
Physical Properties	Refractive Index	2.356
	Solubility in water	Insoluble
	Appearance	Grey-white to yellow powder
	Odour	Sulphurous odour

3. PREPARATION TECHNIQUE: CHEMICAL BATH DEPOSITION (CBM) METHOD

In this review, we confined our discussion on the deposition of ZnS thin films mainly by the CBD technique. Then, based on CBD techniques, a collection of various preparation procedures and deposition of ZnS thin film available in recent days are given in table 3. Moreover, this method gives stable, adherent, uniform and hard films with good reproducibility by a relatively simple process, only it requires a small and portable apparatus (figure 1) setup. And during deposition, for the shaking of sample compartment, closed and isolated apparatus is more desirable to become an impurity-free thin film preparation.

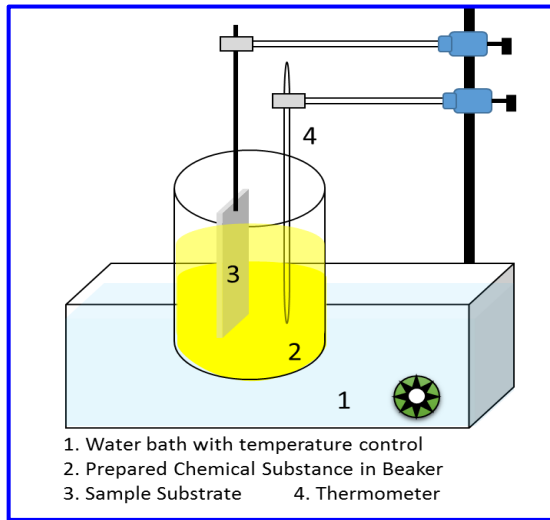


Fig. 1: Schematic diagram of CBD Method

Deposition of ZnS thin film by CBD method refers to the main reaction between Zn^{2+} and S^{2-} ions. The precursors of zinc solution are commonly zinc acetate $[Zn(CH_3COO)_2]$, zinc sulphate ($ZnSO_4$), or zinc chloride ($ZnCl_2$) and most preferably thiourea $[CS(NH_2)_2]$ used as sulfur ions reagent, then both are mixed together and hence it called as one-pot preparation method. In addition, to maintain a constant pH value, one or more complexing agents such as ammonia solution (NH_4OH), tri-sodium citrate (TSC) ($Na_3C_6H_5O_7$), triethanolamine (TEA) ($C_6H_{15}NO_3$), Na_2 -EDTA ($Na_2C_{10}H_{16}N_2O_8$) or hydrazine hydrate (HH) (N_2H_4) are used and to form a uniformity of as-prepared ZnS thin films. Even though, the purity of chemicals is another essential factor. Therefore, all the researcher who wish to bring out good research, to consciousness the above factors, it may have an effect on the significant results.

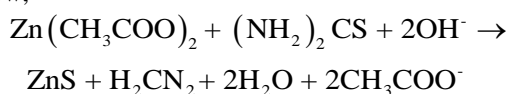
Table 3. Details of Recent Investigation on Preparative Conditions and Properties of ZnS thin films by CBD method

Bath Composition	pH Value	Prepared film thickness (nm)	Deposition of		Selected Substrate	Remarks	Reference
			Temp (°C)	Time			
$ZnSO_4$, $CS(NH_2)_2$, NH_4OH , $N_2H_4.H_2O$	-	-	70	2 h	Soda-lime glass	-	(Wei et al. 2013)
$ZnSO_4$, $CS(NH_2)_2$, $N_2H_4.H_2O$	-	-	80	40 min	Microscopic glass	-	(Mukhamale et al. 2013)
$ZnSO_4$, $CS(NH_2)_2$, NH_4OH	10	-	80	1 h	Glass	-	(Al-khayatt et al. 2014)
$ZnSO_4$, $CS(NH_2)_2$, NH_4OH	-	-	80	2h	Glass	-	(Zhou et al. 2009)
$ZnSO_4$, $CS(NH_2)_2$, $Na_2C_4H_4O_6$	2, 3, 4	759.7	80	100 min	Glass	-	(Min et al. 2011)
$ZnCl_2$, $CS(NH_2)_2$, NH_4OH , $N_2H_4.H_2O$	10-11.5	600 to 320	90	3 h	Glass	Transmittance=70% and $E_g=3.78$ to $E_g=3.67$ eV	(Ben Nasr et al. 2006)
$ZnCl_2$, $CS(NH_2)_2$, NH_4OH , $N_2H_4.H_2O$	11.5	-	90	3 h	Glass	-	(Eid et al. 2010)
$ZnCl_2$, $CS(NH_2)_2$, NH_4OH , $N_2H_4.H_2O$	11.5	-	90	1-3 h	Glass	-	(Salim et al. 2012)
$Zn(CH_3COO)_2$, $CS(NH_2)_2$, NH_4OH , $N_2H_4.H_2O$	8-9	84-85	70	24 h	Glass	-	(Sarma et al. 2015)
$Zn(CH_3COO)_2$, $CS(NH_2)_2$, $C_{10}H_{14}N_2Na_2O_8.2H_2O$	-	60	80	1 h	Glass	$E_g=3.75$ eV	(Mallick et al. 2019)
$Zn(CH_3COO)_2$, $CS(NH_2)_2$, NH_4OH	10.5	1300	30	3 days	Glass	$E_g=3.851$ eV	(Mukherjee et al. 2015)
$ZnSO_4$, $CS(NH_2)_2$, NH_4OH	-	70, 89, 118, 160 nm	65, 70, 75, 80	20, 30, 40, 50 min	Glass	$E_g=4.05 - 3.97$ eV ZnS NPs radius = 1.9, 2.3, 2.45, 2.51 nm	(Zein et al. 2019)
$ZnSO_4$, $CS(NH_2)_2$, NH_4OH , $N_2H_4.H_2O$	-	-	80	10 – 60 min	Silicon	Substrate tilting angle = $30^\circ - 60^\circ$	(Gangopadhyay et al. 2004)
$Zn(CH_3COO)_2$, $CS(NH_2)_2$, NH_4OH , $N_2H_4.H_2O$	10	220 nm	80	4 h	Glass	$E_g = 3.53$ eV	(Cheng et al. 2003)
$ZnSO_4$, $SC(NH_2)_2$, NH_4OH , $N_2H_4.H_2O$	-	570 nm	90	1 h	Glass	-	(Kamoun Allouche et al. 2010)
$ZnCl_2$, $SC(NH_2)_2$, NH_4OH , $N_2H_4.H_2O$	-	700 nm		2 h		-	

The main feature of CBD technique is that the reaction starts only when the solution, with the substrate dipped inside the solution which is placed in a bath maintained within a suitable temperature range depending on the demand of material formation. During deposition process, below room temperature (RT) is very difficult to deposit a ZnS thin film by CBD method. An alternatively, a water bath is used for deposition in the CBD process. Hence, in CBD equipment, a container is filled with heated water and then sample is placed in the water bath at a constant temperature over a certain period of time. Therefore, the CBD method has controlled the structural and optical properties of the prepared films by changing the bath temperature, pH value of the prepared solution, stirring speed, concentration of reagents, complexing agent, deposition time and annealing conditions.

4. RESULTS & DISCUSSION - REVIEW OF LITERATURE

Lădar *et al.* 2007 prepared and reported for monolayer and multilayer of ZnS thin films by CBD techniques in the alkaline medium using zinc acetate and thiourea. They employed the sodium citrate as a complexing agent for the preparation of ZnS thin films and reaction was involved in the analysis as given below,



They investigated the influence of the sodium citrate complexing agent for the thickness of ZnS films at constant zinc acetate and thiourea concentration. Also, the concentration of complexing agent influences the film quality and growth rate. Hence, the thickness of ZnS films grown onto glass substrates is dependent on deposition time. For the typical CBD techniques, when the deposition time is double, the thickness does not increase twice. Because, the initial growing rate decreases with time and thickness tends to level off. Moreover, the total deposition time for the monolayer ZnS thin films have smaller thickness than those of multilayer ZnS thin film deposition time also same. They also reported the XRD, photoluminescence of prepared ZnS films. They concluded that the investigations much needed in order to explain the observed properties and to obtain more optimum luminescent ZnS layers.

Gallanti *et al.* 2016 developed the new bath technique for the preparation of photochemical deposition of ZnS thin film on CIGSe substrate for solar cell applications. They studied the effect of the deposition time on the thickness of the deposited films and reported the growth of the films with three steps that are, i) an induction time at the beginning of the process where no observable growth occurs, ii) an approximately linear region and iii) a termination step where no further

growth occurs. They studied the morphology of as prepared ZnS film and deposited on a CIGSe substrate in 25 minutes and then obtained the homogeneous ZnS film with thickness of 20 nm. They also studied the optoelectronic properties of the prepared solar cells performances with the deposition time varied between 10 and 50 minutes. They optimized the best efficiencies for deposition time rate between 25 and 30 minutes. Therefore, they reported that the method has more efficiencies of the solar cell preparations, moreover as prepared solution could be reused four times consecutively, that is the main advantage. Also they mainly achieved the better fill factor and short-current density. Finally, they concluded that the ZnS buffer layer deposition on CIGSe substrate has no need to heat the prepared solution, no need to prevent precipitation of various species using complexing agent and easy implementation for low reactant concentrations.

Ben Nasr *et al.* 2006 reported the pH contribution for the structure and growth of deposited zinc sulphide thin films on glass substrates by the Chemical Bath Deposition technique. They analysed and reported thin films using the XRD, SEM, and optical studies. The researchers analyzed by changing the pH in the chemical bath which were induced the layer of crystallinity of the ZnS thin films and they found the best pH value is 10. In the XRD analysis, they observed the two main peaks at the diffraction angles of 28.8° and 47.7° which are assigned to both cubic and hexagonal phases of the planes (111)^{cub} / (002)^{hex} and (220)^{cub} / (110)^{hex}. Moreover, the other characteristic peaks of (100), (101), (102), (103) and (200) planes of hexagonal are not present in all spectra. And so, the prepared ZnS films having cubic structure (h-ZnS) whatever the tested pH values. Once, it interpreted and they offers the decreasing of film thickness. In the optical transmission analysis, the band gap energy obtained and varies from 3.67 to 3.88 eV. Particularly, the band gap energy equal to 3.78 eV for the crystalline structure of film at pH=10 in chemical bath. Also, it closely agrees the ZnS thin films obtained by CBD technique. Moreover, these studies were shows that the pH contributes the growth and the structure of deposited thin films. They particularly observed and found the best crystallinity of the ZnS thin films pH is 10 and then analysed. In the above study, in order to optimize the process and produce the suitable layer for optical window in solar cells.

Oliva *et al.* 2010 Investigated a single phase ZnS films Prepared by the CBD-method and the prepared films are transparent, pale-white color and good adherence. Under light reflection, these films looks like gold color. The study the structural morphology and optical band gap energy In this work, a methodology to proposed for solar cells applications. This method higher KOH concentrations used for CdS films deposition but changing the pH of the bath Cd salt by a Zn salt. The chemical bath optimal pH=11.5 value with

the KOH reagent. The pH value in the chemical bath, adjusted with KOH in this work, resulted a key factor, because concentrations below 1.0 M do not produce conditions for ZnS films deposition. This effect was also reported by Antony et al. [10] for a chemical bath with $\text{Zn}(\text{NO}_3)_2$ and NH_4OH as the salt reagent and the source of OH radicals, respectively. High quality ZnS films formed the pH value important role for the films formation. Given to annealing treatments at 200 °C and 400 °C on ZnS films in order to studied their effects. Small changes obtained on the optical properties of ZnS films with the annealing treatment, as demonstrate by the reduction of the band gap energy value for higher annealing temperatures. However, we found that the annealing process did not produce important changes on the crystalline structure of the films. Formed a optical direct band gap energy of ZnS films by spectrophotometry technique and calculated from the absorption spectra through the relation:

$$\alpha^2(h\nu) = A^2(h\nu - E_g)$$

where α is the optical absorption coefficient, $h\nu$ is the energy of the incident light, h is the Planck's constant and ν the light frequency. By plotting α^2 vs $h\nu$, the bandgap energy of the initial absorption edge line when $\alpha = 0$. Calculated the ZnS optical transmittance between 70-80% in the visible light spectrum range. The deposited films changes the band gap energy values from 3.70 eV to 3.45 eV for as-grown and for annealed films, respectively. The analysis of the films stoichiometry ratio (Zn:S) close to 1.0:1.2 both for punctual and zone analysis.

Liu et al. 2012 developed the uniform ZnS thin film composed of nanocrystallines with for CIGS solar cell deposited by CBD technique. The deposition morphology, growth rate, structure and optical properties of ZnS thin films within 100 nm thick is investigated by a field emission scanning electron microscope (FE-SEM), transmission electron microscope (TEM), X-ray diffractometer (XRD), atomic force microscope (AFM) and ultraviolet visible light spectroscopy (UV/VIS). The FESEM morphologies images showed that the impact, even and dense ZnS films deposited on soda lime glass used to high concentration ratio of thiourea. The ZnS thin film grow rate is 0.88 nm/min. The TEM diffraction patterns and XRD patterns revealed that ZnS films were nanocrystallines, of which FCC (111) phase dominated over others. The transmittance and band gap of ZnS thin films are over 80% in the range of 300-800 nm and 3.83 ~3.85 eV, respectively. The ZnS/CIGS/FTO structure and Al:ZnO/ZnO/ZnS structure in CIGS solar cell formed by wet processes showed good hetero interfaces.

Zhou et al. 2009 reported the structural characterization of zinc Sulphide (ZnS) thin films deposition by chemical bath deposition (CBD) on glass

substrates. The solution concentration and annealing condition played a very important role on transmissivity, homogeneity, crystal and transmissivity of ZnS thin films. Spectrophotometer, X-ray diffraction (XRD), Scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDS), digital four-point probe resistance measurement were used to characterize their properties and composition.

- The trend of the transmissivity was upward within range of 300–600 nm wavelength of incident light, then it would be stable above 600 nm. Transmissivity of the ZnS films were more than 80%. Transmissivity of the ZnS films without annealing was greater than that of at 200 °C and higher than that of at 300°C for both 1 h. As concentration of ZnSO_4 was lower between 0.020 and 0.030 mol/L, transmissivity of the ZnS film was higher.
- The films' structure was basically amorphous or microcrystalline. After annealing, the main diffraction peaks due to ZnS (111) planes correspond to sphalerite-type ZnS.
- The particles of the films surface were almost spherical and homogeneous, and there were some white spots. Before annealing, ZnS and ZnO were the main composition of the film after annealing.
- The resistance of the ZnS films without annealing reduced with the increasing concentration of ZnSO_4 .

Bian et al. 2008 have adopted the CBD method and used to form a ZnS thin films which was deposited on glass substrates at 80–82 °C temperature. The film deposition is in process, they added the complexing agents namely, ammonia or ammonia-hydrazine hydrate, they influenced the quality of as-deposited films and the substrate was in vibration condition. They reported the role of hydrazine hydrate for the growth of ZnS thin films. It was improved the homogeneity, specularly and the growth rate of films. Also, the addition of hydrazine hydrate led to few white grains of film. Moreover, vibration of substrate was reduced the formation of pinholes and improved the uniformity of the films. They were analysed the physical and optical properties of as-prepared films were characterized using XRD, SEM and UV-vis spectroscopy. From the XRD analysis, ammonia-hydrazine was better complexing agent compared with other agents and it shows the hexagonal crystallization structure with (008) diffraction peak. The prepared ZnS films exhibited good optical properties with high transmittance (~80%) in the visible region and the band gap value was estimated in the range of 3.5–3.70 eV.

In 2017, González-Chan et al. 2017 have been analysed the physicochemical process for the performance of zinc Sulphide (ZnS) thin films by chemical bath deposition (CBD). They have investigated the performance of the ZnS solution

contained zincchloride, potassium hydroxide, ammonium nitrate and thiourea. These chemical compound permitted the physicochemical analysis of ZnS thin film deposition. Then the solubility curves and species distribution diagrams have been utilized to obtain the best conditions for ZnS thin film deposition and the various concentration of the bath temperatures in the range of 25 to 90 °C at different deposition time rate (González-Panzo *et al.* 2014). The results were indicated that the necessity to adjust the thiourea solution concentration according to the bath temperature. It helps the formation of ZnS thin film deposition in order to contribute with enough amounts of sulfur ions in the bath solution. They also reported the thiourea concentrations with respect to the bath temperatures like 2.25 M (25 °C), 1.25 M (40 °C), 0.6 M (60 °C) and 0.2 M (90 °C). The impact of thiourea at low concentration, the formation of ZnS thin films has poor quality due to the excess of zinc hydroxi-complexes. Moreover, the detailed relative properties such as optical, stoichiometric and morphological have been reported at different concentration of thiourea.

Sample prepared at	Thiourea concentration	Zn/S ratio	Bandgap Energy
25 °C	2.25 M	0.96	3.72 eV
40 °C	1.25 M	0.90	3.69 eV
60 °C	0.60 M	1.11	3.66 eV
90 °C	0.20 M	1.15	3.65 eV

The ratio of Zn/S has close to 1 and homogeneous surfaces with similar grains size, optical transmission between 80 and 85%, and bandgap energy has close to the bulk value of 3.72 eV were obtained for all the thin films deposited with the proper conditions of thiourea at different concentration with four different temperatures such as 25 °C, 40 °C, 60 °C and 90 °C with optimized deposition time rate. Thus, as deposited ZnS thin films has good quality at the wide range of bath temperatures if adequate chemical conditions are required. Finally, they reported that the solubility curves and species distribution diagrams proved the best physicochemical conditions.

Patel *et al.* 2018; Khatri *et al.* 2018 investigated properties of the ZnS thin films deposited on glass substrate by using CBD technique at bath temperature 70 °C with the effect of post annealing at 350°C temperature for 1 hr. XRD confirms hexagonal phase for both as-grown and annealed ZnS thin films. The average crystallite size is 331 nm for as-grown and 643 nm for annealed thin films using Debye-Scherrer equation. TGA analysis shows that 350 °C is suitable for annealing process of ZnS thin film and optical measurement shows that the transmittance of film has in the range of 5-35% in the visible region. Also, the films have direct bandgap, which increased from 3.80 eV to 4.18 eV with annealing at 350 °C for 1 hr. Finally they

reported that the materials have potentially used in electroluminescence devices and photovoltaic cells.

For doping on ZnS, as-prepared thin films have been developed for huge number of applications. Doped ZnS may have either cubic or hexagonal structure as zincblende (ZB) or wurtzite (WZ), which depends on its synthesis conditions like sample prepared temperature, precursor type and concentration. For example, Co, Cu, Fe and Sn doped in ZnS thin film properties have been tabulated as follows (Shakil *et al.* 2018),

Table 4. Comparison of (Cu, Ni, Co, Fe) doping in ZnS for some properties (Mukherjee *et al.* 2017; Shakil *et al.* 2018)

Property	Co-Doped	Cu-Doped	Fe-doped	Sn-Doped
Atomic no	27	29	26	50
Band Gap (eV)	3.6	3.47	3.94	3.90
Crystallite Size (nm)	12	11	10.38	12
Structure	Zincblende (ZB)		Wurtzite(WZ)	
Structure type	Cubic		Hexagonal	

From table 4 inferred that due to change of doping element, the energy band gap, structure as well as crystallite size may vary with respect to the selection dopant also it may vary with the concentration of doping element also.

5. CHARACTERIZATIONS OF THE FILMS MEASUREMENT OF FILM THICKNESS

Film thickness have measured with different methods as surface profiler, gravimetric method, etc. Generally, film have been deposited on only one side substrate and thickness is calculated by (Oriaku *et al.* 2008).

$$t = \frac{m}{\rho A}$$

Where, m is the mass of the deposited film measured with a very sensitive electronic balance, A is the area and ρ is the density of the film obtained from crystallographic data.

5.1 X-ray Diffraction (XRD)

Grain size of the crystalline structure of the prepared film is obtained by substituting values of Full Wave Half Maximum (FWHM) to the well-known Debye-Scherrer formula (Jones *et al.* 1938):

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where D is crystalline size, K is the Scherrer constant (= 0.94), λ is the wavelength(=1.54059Å) of the X-ray source used, β is the full width at half maximum

intensity in radians (FWHM) and θ is the angle of diffraction at the peak or Bragg angle.

5.2 Lattice Constant

The lattice constant for both doped and undoped thin film were determined from the relation

$$a = d\sqrt{(h^2 + k^2 + l^2)}$$

where d is the spacing between the crystal planes. The lattice parameter a , for ZnS structure was obtained from the d interplanar spacing of different peaks by the equation:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

The precise value of lattice parameter a can be estimated from Nelson-Riley function (Long et al. 2008):

$$F(\theta) = \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta}$$

Where θ is the Bragg angle.

5.3 Optical Characterizations

1. Absorbance of the Film: The spectrophotometer used to obtain the optical information for the absorbance of the film. The absorbance α is obtained from the relation:

$$\alpha = \frac{2.30A}{t}$$

Where, t is the thickness of the deposited film, A is the absorbance and reflectance is neglected for highly transmitting film.

2. Bandgap Estimation:

The bandgap of materials is a very important parameter that determines the application of the films. It is evaluated using the formula (Ezekoye et al. 2005).

$$\alpha = \left(\frac{A}{h\nu} \right) (h\nu - E_g)^n$$

Where, $n=1/2$ for allowed direct bandgap transition materials. The plot of α^2 or $(\alpha h\nu)^2$ versus photon energy $h\nu$ (in eV) with extrapolation of the straightline portion of the curve to zero shows that the absorption coefficient ($h\nu$ axis) gives the direct bandgap energy of materials. When $n=2$ shows that the allowed indirect bandgap transition materials. The plot of $\alpha^{1/2}$ or $(\alpha h\nu)^{1/2}$ versus photon energy $h\nu$ (in eV) with extrapolation of the straightline portion of the curve to zero shows that the absorption coefficient ($h\nu$ axis) gives the indirect

bandgap energy of materials. When $n=2/3$ indicates that forbidden direct transition and $n=3$ for forbidden indirect transition (Ezekoye et al. 2005).

5.4 Optical Measurement

Ultra violet - visible region spectrometer operated in the wavelength range of 400-700 nm. The optical absorption coefficient, α , was calculated from the values of T and R using the following relation (Ezekoye et al. 2005)

$$\alpha = \frac{1}{t} \ln \left[\left(\frac{(1-R)^2}{2T} + \frac{(1-R)^4}{4T^2} + R^2 \right)^{1/2} \right]$$

Where, t is the film thickness and k is the extinction coefficient $\left(k = \frac{\alpha \lambda}{4\pi} \right)$. The refractive index, n then can be calculated using the relation:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$

The spectral variation of the refractive index n and extinction coefficient k for ZnS films of different thickness. It is seen that the refractive index of ZnS films increase with the increase in the film thickness. In order to deduce the band gap of the thin films, the absorption coefficient of the investigated ZnS films was analyzed using the following equation (Pankove et al. 1971):

$$(a\hbar\omega) = A(\hbar\omega - E_g)^p$$

Where $\hbar\omega$ is the photo energy, A is a parameter that depends on the transition probability, E_g is the optical band gap and the exponent p depends on the type of the optical transition between the valence and the conduction band, direct or indirect transition (Pankove et al. 1971).

5.5 Applications of Zinc Sulphide thin film

It has numerous applications such as ZnS nanostructures as field emitters, field effect transistors (FETs), catalyzers, Fuel cell, Electroluminescence devices, Solar cells, UV-light and chemical sensors, humidity and gas sensors, biosensor and nanogenerators etc.

6. CONCLUSION

The present review paper describes the comprehensive literature study for the necessary background theory of ZnS thin film deposition. Also this paper describes the chemical bath deposition method in detail for well-adherent and uniform zinc sulphide (ZnS) thin films formation. CBD deposition

technique parameters, ZnS thin film prepared previously and the results of structural, morphological, optical, electrical properties etc., have been successfully discussed. Moreover, the mathematical relations are given for the measurement of prepared thin films to achieve the related property of such applications.

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